Stabilization of Polypropylene for Rotational Molding Applications

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Abstract: Rotational molding (RM) is a useful process for making large hollow objects. Due to its relatively high toughness and forgiving thermal oxidative degradation behavior, polyethylene is a most widely used material. However, it has too low elastic modulus for some important applications which leads to adaptation of polypropylene (PP) as a RM material. PP requires specially tailored antioxidant (AO) packages if it is to have any chance of surviving the often long (up to ca. 30 minutes) cycle times associated with RM. During the study the addition of the following stabilizers and antioxidants (AO) to the PP copolymer were investigated: a hindered phenolic primary AO, a phosphite secondary AO, a thioester secondary AO and a hindered amine light stabilizer. Synergistic effects between the primary and secondary AOs, as well as optimum heating times, were investigated. During the investigation formulations were prepared by compression molding and bench-scale RM. The combination resulting in the most effective synergism is the hindered phenolic primary antioxidant combined with the phosphite secondary antioxidant. A gel silica controlled release agent for the stabilizers was also investigated but did not yield significant improvements in stabilization.

Keywords: Polyolefins, Rotational Molding, Antioxidants, Thermal Oxidation.

1. INTRODUCTION

Rotational molding (RM (or rotomolding)) is a plastics processing method that is used to produce large hollow plastic parts. During the process, a charge of plastic powder is placed inside the mold, which is then closed and rotated slowly around two axes. The mold is heated to ensure that the charge melts and forms a coating inside the surface of the mold. The mold continues to rotate after it is removed from the oven. When the plastic charge is sufficiently cooled and solidified, the final plastic part is taken from the mold [1]. RM is unique in that the plastic particles are not subjected to any shear forces while they are melting. Sintering of the polymer particles is dependent on the intensity of the thermal motion and mobility of the polymer chains. Parts and products made by rotational molding can be competitive with those made by other processes, while the process also offers some unique processing advantages [2].

Polyethylene is the material currently employed for most RM applications. However, new materials such as polypropylene (PP) have the potential to allow the growth of new applications and can potentially be modified to be suitable for RM. Despite both materials being polyolefins, PP suffers much more from thermo-oxidative degradation than polyethylene due to its easily abstractable tertiary hydrogen atom. All the polymers from this family are susceptible to degradation, especially if the processing method employs long heating times (in RM, typically in excess of 20 minutes) [3, 4]. High temperatures can lead to reactions which can change different aspects of the polymer, such as its mechanical properties or even its molecular mass. In PP, chain scission and the reduction of the molecular mass are observed at high temperatures, contrary to the case for polyethylene [5, 6]. Hence, antioxidants are necessary for all PP applications and the selection of such ingredients is an important factor in determining the success in any given commercial application of the material. For optimum processing stability, a single antioxidant of the phenol-alkane type tends to give the best results [7, 8]. However, for long term service stability at high temperatures it is more common to employ a synergistic mixture. Prolonged oven heating of

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E-ISSN: 1929-5995/15

polypropylene leads to embrittlement, thus embrittlement time is useful to measure the efficiency of the antioxidant. Antioxidants can be successful in very small quantities. Usually 0.05-0.25% of an antioxidant by weight of the polymer should be enough to obtain an appropriate result, although for some applications the antioxidant level may exceed to 0.8% [9].

Hindered phenolic compounds are the preferred type of primary antioxidants for thermoplastics. They are hydrogen donors and remove chain breaking radicals from the system, as well as preventing the loss of the tertiary hydrogen from the PP backbone, so propagation is suspended or delayed. The most familiar hindered phenol is butylated hydroxytoluene, also known as BHT. Although BHT is a very effective chain terminator, it suffers from high volatility, which makes it unsuitable for high temperature applications. Hence hindered phenols with higher molecular mass are required e.g. longer chain phenolic antioxidants [10-12]. Secondary antioxidants inhibit oxidation by decomposing hydroperoxides, and reducing the hydroperoxide to more stable products, such as alcohols. Unlike primary antioxidants, they are inadequate if used alone, so they are typically used in combination with primary antioxidants to obtain synergistic effects.

The fundamental problem investigated in this paper is whether polypropylene could be sufficiently stabilized by one, or a combination of antioxidants and light stabilizers to render it suitable for RM applications. Two of the most common secondary antioxidants, phosphites and thioesters, will be utilized in the investigation in combination with a primary antioxidant [13-16]. Hindered amine light stabilizers, as well as being UV stabilizers, can also be effective as heat stabilizers, despite their behavior being quite different from hindered phenolic compounds. The synergistic effect between these two types will also be investigated [7]. The investigation will demonstrate that, contrary to conventional wisdom, a suitably stabilized PP can be applied successfully in roto molding applications.

2. MATERIALS

A well-established, popular commercial hindered phenolic antioxidant was used as primary antioxidant in this study.In addition, two secondary antioxidants were also evaluated, one a popular phosphite type and the other a widely used thioester. The fourth type of stabilizer investigated was a widely used polymeric hindered amine light stabilizer (HALS). Both the secondary antioxidants and the HALS were used as synergists in combination with the primary hindered phenolic antioxidant.

A gel silica was used as a controlled release agent. It is a medium pore sized calcined silica gel which is known to have a large quantity of isolated silanol groups on its surface. This material was added to the polymer matrix with the antioxidant combination in order to see if it could extend the thermal stabilization.

A commercial polypropylene copolymer was used with a medium melt-flow rate (MFR) in the range 10 – 40 dg/10 min (230°C, 2.16 kg) and a density of 900 kg/m^3. It contained a tailored and purpose made stabilizer package.

3. EXPERIMENTAL SECTION

3.1. Preparation Stabilized Formulations and Test Pieces

Degradation analysis samples were prepared using a Thermo Haake Rheomix 600 mixing bowl fitted to a Thermo Haake Polydrive dynamometer unit. The bowl was fitted with roller type rotors. The mixing was carried out for 5 minutes and the specific antioxidant concentration were introduced to the polymer matrix at the end of the first minute. The mixing was carried out a set chamber temperature of 180°C, with a rotor speed of 70 rpm. The Polydrive software generated graphs of mixing torque and melt temperature versus mixing time. Values of the mixing torque and melt temperature were recorded for each sample.

After removing the mixing sample from the Rheomix chamber, it was transferred to a 50 ton electrically heated hydraulic press to be compression molded. The heated platens were set at a temperature of 180°C and after 10 minutes the samples were transferred to a second 50 ton press with water cooled platens for the cooling of the sample. Once the plaque is obtained, it is cut into 2 cm x 2 cm squares with a band saw.

The formulations to be rotomolded were prepared by twin screw extrusion using a Thermo-Prism TSE HC24 twin screw extruder fitted with a Brabender gravimetric feeder. The temperature profile is described in Table **1**. Head pressure was nominally 14 bar and the screw speed was of 200 rpm, with the feed rate 10 kg/h. The resulting molten polymer was extruded through a two-hole die and cooled by passage through a water trough before being pelletized.

Table 1: Temperature Profile of Twin Screw Extruder

Temperatures (°C)						
Feed Zone	Mixing and Kneading					Die
	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	
170	200	210	210	180	180	220

A bench-scale Rotomolding machine was used to prepare samples molded at different molding times for impact strength assessment. The oven temperatures used to rotomold the specimens were between 160°C to 230°C. Temperature and timing were regulated manually. The mold for the machine was made of cast aluminum, lined with a polytetrafluoroethylene powder coating, and its size was: 8cm x 25cm x 8cm. Impact strength specimens were cut manually with a band saw from the side of the rotomolded pieces. The nature of the molding process at this scale caused the specimens to have slightly different wall thicknesses. The latter however, was taken into account in the expression for impact strength and the variation was not so great as to cause significant geometric effects on impact strength.

3.2. Melt Flow Rate (MFR) Determination

The melt-flow rate (MFR) of the formulations prepared by twin screw extrusion was determined using a Ray-Ran melt-flow indexer at 230°C with a 2.16 kg load.

3.3. Impact Strength Measurement

Unnotched Charpy impact strengths of the composite test pieces were measured using a Zwick 5102 pendulum type impact testing apparatus equipped with a 4 J striker and a 40 mm span between sample supports. Each test was carried out at ambient temperature (21°C ± 1°C). Eight replicate tests were done for each composite sample, calculating the average value and the standard deviation.

3.4. Aging Methods and Monitoring of Oxidation Using FTIR

Thermal oxidative aging of the Haake mixed and compression molded sample plaques was carried out in the melt state at 230°C in a fan–assisted laboratory oven. Samples were placed in aluminum trays prior to oven aging. Samples were taken out from the oven every three minutes in order to see how the carbonyl induction time (CIT) changes with the antioxidant concentration [17].

Aged samples were checked for oxidation at regular time intervals using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The instrument was a Thermo-Nicolet 380 fitted with a Smart-Diamond single bounce ATR. Spectra were made up of 32 scans with resolution set to 4 cm^{-1}. Samples were held against the internal reflection element using the integral clamping system.

Oxidation of PP is manifested by the development of a group of carbonyl absorption bands in the range 1500 cm^{-1} to 1800 cm^{-1} [18] and the development of OH stretching bands (3600-3200 cm^{-1}) due to formation of hydroperoxides and other OH functional species. Formation of carbonyl groups was reliably monitored using FTIR, as this area of spectrum was relatively free of other absorptions and carbonyl growth was more prolific than that of hydroperoxide. Carbonyl peaks tend to appear around 1710 cm^{-1}, but it could extend from 1800 cm^{-1} to 1500 cm^{-1} because of the variation of the degradation products. The analysis of the polymer at regular intervals during the bench scale rotational molding trials can provide information on the increase of carbonyl peak concentrations over the processing time [19].

To determine the carbonyl concentration of the polymer, it is necessary to choose an internal standard band in the polymer spectrum. The internal standards are peaks that remain unchanged during the degradation of the polymer. There are many peaks that can be useful as internal standards for polypropylene: 840, 1166, 1455, 2720 and 2780 to 3000 cm^{-1}, have been popular choices. Some of the latter, however, are affected by crystallization of the PP, and others overlap with several other peaks. The absorption peaks at 2720 and 2780-3000 cm^{-1} can be considered as a safe choice for use as an internal standard and can be assigned to symmetric and asymmetric methylene (CH-H) and methyl (CH_2-H) stretching, as well as CH bending [20].

Once the internal standard is chosen, the carbonyl index (CI) can be measured. This was determined by dividing the area of the carbonyl absorption peaks

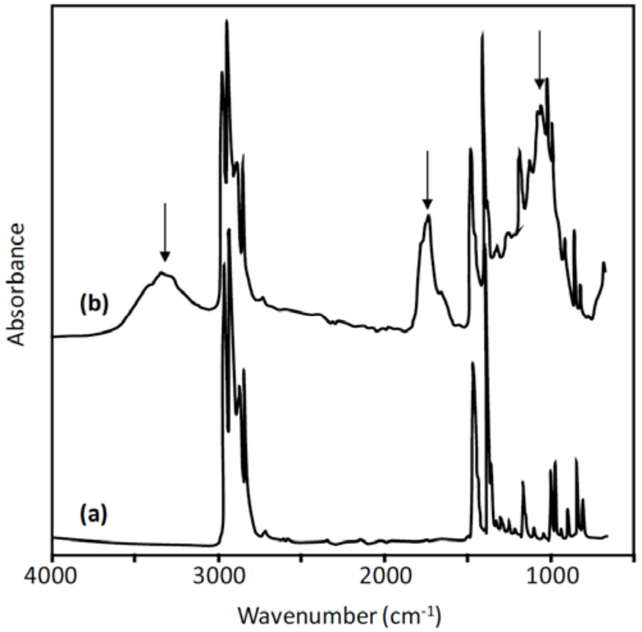

Figure 1: Typical infrared spectrum of PP; (a) Before thermal oxidation and (b) after thermal oxidation. The arrows (from left to right) indicate the hydroperoxides, carbonyl and associated C-O absorptions, respectively.

($A_{C=O}$) at (1500-1800 cm^{-1}) by the area of the internal standard ($A_{C\text{-}H}$) (C-H stretching) peaks (2780-3000 cm^{-1}) (See Equation 1). A plot of CI versus time can be used to determine the carbonyl induction time. The effects of the antioxidants in delaying the onset of degradation can thus be followed graphically.

$$CI = \frac{A_{C=O}}{A_{C\text{-}H}} \quad (1)$$

4. RESULTS AND DISCUSSION:

The results are discussed in several sections. Investigating synergistic or antagonistic mixtures of the primary antioxidant and combinations of the other antioxidants, together with the necessary adequate concentration(s) thereof for RM applications, were considered first.

4.1. Stability and Synergism Aspects

Figure **2** shows that time to onset of carbonyl growth (the carbonyl induction time CIT) at 230°C, increased linearly with increasing primary hindered phenolic antioxidant (1°PhAO) level before reaching a limiting value of ca. 70 minutes at 1°PhAO levels beyond ca. 13250 ppm (ca. 1.33 wt% of PP). The limiting value may be related to stabilizer dispersion / solubility aspects; poorly dispersed / insoluble stabilizer will not be accessible to free radicals. Furthermore, there may be a limiting number of free radical fragments permissible in the polymer due to stationary state effects; i.e. the rate of production of radical fragments (initiation) is precisely balanced by their rate of their annihilation (termination). The dispersion argument could be explored further by monitoring by microscopy and used of more intensive (higher shear) mixing. If the solubility limit has been reached then more intensive mixing should make no difference.

Nevertheless, 70 minutes (at 230°C) is certainly beyond the duration of most PP rotomolding (RM) operations, with the exception of very large components. Therefore the results obtained show that it is possible to usefully increase the processing stability of PP to a level sufficient for RM, albeit at the high cost of very high AO levels. The molding time typical for most PP RM components is about 30 minutes; therefore a 6000 ppm loading of 1°PhAO is arguably sufficient to ensure sufficient thermal stabilization during the process. Furthermore, primary antioxidants are not cheap, so it makes commercial sense to limit the dosage if possible. Bearing in mind the level of stabilization obtained, a 6000 ppm addition is reasonably economical. However, other rotational molding studies [21] in which stability was investigated, used a lower concentration of primary antioxidant. Usually dosages range from 400 ppm to 1750 ppm and combine primary and secondary antioxidants. However, they cannot stabilize the polymer longer than 20 minutes at peak internal air temperatures of 230°C. In some studies [22], primary antioxidant concentrations of 1% (w/w) (10000ppm) were utilized and the stabilization obtained was excellent.The economics of such high doses is, however, open to question.

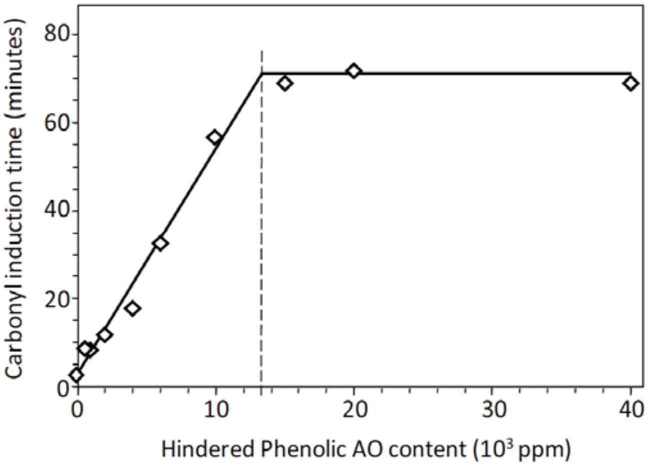

Figure 2: Carbonyl induction time versus hindered phenolic anti-oxidant concentration.

Table 2: Stabilizer Formulations and Associated Carbonyl Induction Times (See Final Column). The total Concentration of Antioxidant is 6000 ppm

Hindered Phenolic Antioxidant (%)	Hindered Amine Light Stabiliser (%)	Phosphite Secondary Antioxidant (%)	Thioether Secondary Antioxidant (%)	CIT (min)
0.0	100.0			3
12.5	87.5			6
37.5	62.5			9
50.0	50.0			9
62.5	37.5			15
87.5	12.5			24
100.0	0.0			33
0.0		100.0		12
16.7		83.3		33
33.3		66.7		33
50.0		50.0		42
66.7		33.3		42
83.3		16.7		36
100.0		0.0		33
70.0			30.0	21
75.0			25.0	24
80.0			20.0	30
85.0			15.0	21
90.0			10.0	27

Generally, thioester antioxidants work well with in conjunction with 1° PhAOs. However, other secondary antioxidants such as phosphites can also be utilized, as well as hindered amine light stabilizers (HALS). The latter do not only improve stabilization against UV radiation, they can also improve resistance to thermal oxidation. From the data obtained during the first part of this thermal oxidative ageing study, it was decided to fix the total stabilizer concentration by mass to 6000 ppm. A range of combinations were investigated in order to evaluate and compare the differences between stabilizers, as well as any potential synergism between these stabilizers. This data can help to determine which combination of the 1°PhAO and secondary antioxidant will provide the best resistance against thermal oxidation.

The carbonyl induction time increases when higher 1°PhAO concentrations are added to the polymer matrix in the combination with the hindered amine light stabilizer. This indicates weak antagonism between these two antioxidants, because the longer induction time can be ascribed to the increasing levels of primary antioxidant. Anyway, the hindered amine light stabilizer is not primarily added to increase resistance against thermal oxidation, but to provide improved stability against UV radiation. It can provide some stabilization when aldehydes and peracids are present, generally at low temperatures, and several previous reports [7, 23] described how the HALS could be used as long term stabilizer and even become more efficient than hindered phenolics to reduce thermal degradation. However, in RM high temperatures are involved and therefore the HALS would not be suitable for this application.

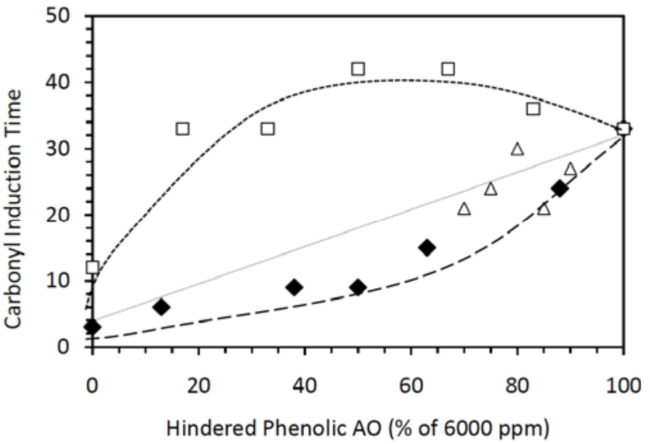

Figure 3: Carbonyl induction time (CIT) versus stabilizer composition; ◆ hindered phenolic – HALS, ☐ hindered phenolic - phosphite, △ hindered phenolic - thioether. The total amount of antioxidant added to the polymer matrix is 6000 ppm and the x-axis numbers represents the percentage of hindered phenolic antioxidant in the combination.

The phosphite antioxidant performed better than the HALS with the 1°PhAO and displayed some degree of synergism. The best stabilization is obtained with a

60% 1°PhAO/ 40% secondary phosphate mixture. However, the combination of 20% 1°PhAO/ 80% phosphite antioxidant also provides a reasonable degree of stabilization, and it will be economically the cheaper option because phosphite antioxidants are cheaper than hindered phenolic ones.

Jones *et al*. [24] investigated polypropylene stabilization with a broadly similar type of primary hindered phenolic antioxidant and thioether secondary antioxidant and analyzed five different combinations. These authors reported that the best stabilization was provided by the combination of 80% primary hindered phenolic antioxidant and 20% secondary thioether antioxidant. However, their study was focused more on long term thermal stability and it used 4000 ppm concentration by mass in total. Since the current investigation deals with rotational molding applications, it was decided to use the 80:20 combination as the entry point formulation. It was found that the 80:20 combination indeed provided the best stabilization. When considering all three secondary antioxidants, the thioester began to lose its efficiency above 160°C.

In this study, the secondary phosphite antioxidant would therefore be the best synergist when combined with 1°PhAO. The combination containing 1°PhAO at 66.7% and the secondary phosphite antioxidant at 33.3% at a total concentration of 6000 ppm was therefore chosen for further MFR and RM studies. A formulation containing only the 1°PhAO was prepared as a control. The gel silica controlled release agent was be added to all the mixtures in the same amount as the antioxidants (6000 ppm).

4.2. Melt Flow Rate (MFR) Measurements

After the samples were melt-blended using the Thermo-Prism HC24 twin screw extruder, MFR measurements were carried out. The MFR data is shown in Figure **4**. The MFR of all the formulations (including the control with no additional stabilizer added) decreased by the same extent after melt blending, which is unusual for PP. Due to the tertiary hydrogen, PP and PP rich formulations usually undergo chain scission during melt processing [21, 25]. The observed uniform decrease may be indicative of effective stabilization of the control or the copolymer (or blend) containing so much ethylene (or ethylene rich copolymer) that cross linking simply dominates chain scission. However, the addition of antioxidants and additives could induce a substantial reduction of the MFI, as reported by Peltzer *et al*. [26]. The results obtained provide proof that the antioxidants are efficient and that the polymer matrix is protected adequately.

It is important to bear in mind that the process of RM generally requires low melt viscosity to enable fusing of the polymer particles at zero pressure and near zero (or zero) shear rate. Despite the necessity of antioxidants for the stabilization of the PP, the observed decrease of the MFR may not be conducive to fusion of PP particles during the RM process. Further study is required to verify this as the zero shear rate behaviour cannot be predicted from MFR data.

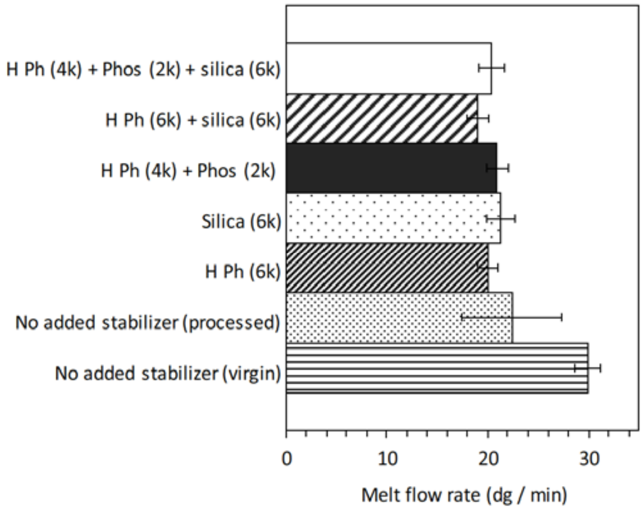

Figure 4: Melt flow rate data (230°C / 2.16 kg) for twin extruded samples with the indicated stabilizer compositions; H Ph – hindered phenolic antioxidant, Phos – phosphite secondary antioxidant. The numbers in parenthesis indicate the addition levels in 1000s (k) of ppm.

4.3. Rotational Molding Studies

4.3.1. Degradation Assessment for Rotomolded Specimens

The CI of samples cut from the rotomoldings were determined as a function of molding time; note the time taken to produce a fully fused molding was 18.5 minutes. It should be noted that the internal air temperature of the mold increased with molding time as the mold was rotated in the oven; the nominal internal air temperature was, however ca. 230°C, the latter was never exceeded.

For the reference materials without any additional stabilizer, it is evident that the carbonyl index (CI) increases with increased molding time, with the increase being particularly rapid for the sample not containing the high surface area gel silica. Addition of 6000 ppm of the 1°PhAO provided very effective stabilization, because the CI increased only slightly to a limiting value after ca. 20 minutes of heating and did not vary much over the molding time range investigated. The combination of the 1°PhAO and the controlled release silica agent initially improved stabilization, but after 25 minutes of molding time the data converged with, and then slightly exceeded, that for 1°PhAO alone. Although some synergism has been observed earlier between the 1°PhAO and the secondary phosphite-based antioxidant combination, it was only marginally more effective than the sample containing 1°PhAO only. Addition of 6000 ppm high surface area gel silica (a possible controlled release reservoir) to this combination gave a marginal improvement up to ca. 22 minutes molding time. Thereafter, the performance deteriorated relative to when the silica release agent was absent from the formulation. It is therefore apparent that the controlled release system does not function properly in this formulation at extended molding times. This may be due to the balance of interaction strengths between the silica release agent and the antioxidants and stabilizers being unfavorable. Previous work [27] has reported that gel silica does not improve thermal ageing of PP when a single antioxidant is used. When synergistic antioxidant combinations are used, stabilization performance depends on the structures of the antioxidants and their relative strength of interaction with the silica surface.

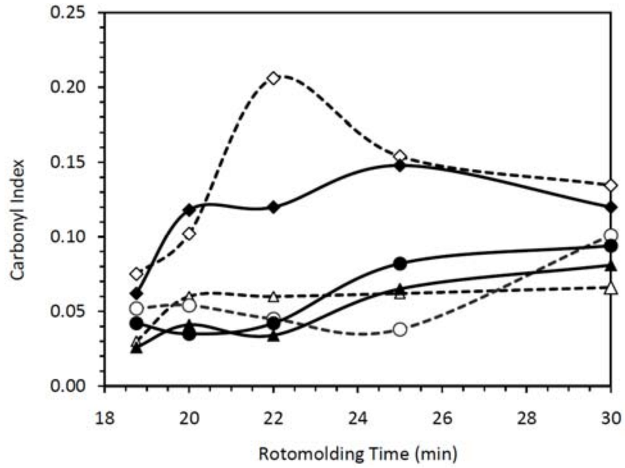

Figure 5: Carbonyl index of rotational moldings versus molding time for the stabilizer different combinations. ◇◆ unstabilized, △▲ hindered phenolic antioxidant, ○● hindered phenolic antioxidant combined with phosphite secondary antioxidant. Open symbols represent combinations without silica, solid symbols represent combinations with silica.

4.3.2. Impact Strength of Rotomolded Specimens

Un-notched impact strength versus molding time data is shown in Figure **6**. All formulations apart from the no added stabilizer ("unstabilized") control, had initial (at 18.5 minutes molding time) un-notched impact strength values between 20 and 30 kJ m^{-2}. The 1°PhAO/phosphite combination was marginally the best within this range, followed by the 1°PhAO alone and the 1°PhAO/silica. Then followed the silica alone and the 1° PhAO/phosphite/silica combination. After 22 minutes molding time the impact strength of the 1°PhAO alone, 1°PhAO/silica and 1°PhAO/phosphite/ silica combinations held relatively steady between 20 and 30 kJ m^{-2}, whilst the 1°PhAO/phosphite combination increased to 32 kJ m^{-2} and the formulation containing the silica only already plummeted to 4 kJ m^{-2}. At 25 minutes molding time, the 1°PhAO/phosphite combination showed the best performance (35 kJ m^{-2}) followed by the 1°PhAO alone (30 kJ m^{-2}) and the 1°PhAO/phosphite/silica (18 kJ m^{-2}). The worst performers (ca. 5 to ca. 2 kJ m^{-2}) at this point were the unstabilized, silica and 1°PhAO/silica samples. Somewhat surprisingly, the best performer at 30 minutes molding time was the unstabilized control (13 kJ m^{-2}), the worst performer was the 1°PhAO/silica combination (2 kJ m^{-2}).

The effect of the silica on the impact performance is likely to have been dominated by excessively strong adsorption of the 1°PhAO by the silica; the impact strength held between 20 and 30 kJ m^{-2} until 22 minutes and then dropped off sharply thereafter. The 1°PhAO/phosphite/silica combination gave relatively steady impact strength but the initial value was rather low (ca. 21 kJ m^{-2}). The last value however, obtained at 30 minutes molding time, was ca. 8 kJ m^{-2}. The latter is slightly better than for the formulation without silica (ca. 4 kJ m^{-2}). The 1°PhAO/phosphite/silica combination arguably shows weak controlled release. Further investigation is clearly required to fully exploit the rather weak potential seen here. In previous studies [28, 29] the controlled release is thought to be brought about by the displacement of a more weakly adsorbed stabilizer by one which adsorbs to the silica more strongly; the latter was shown to be true for Irganox 1010/Chimassorb 944 combinations in film grade polyethylene [29]. The Chimassorb 944 was thought to displace the slightly more weakly adsorbing Irganox 1010 [28, 29]. In the present study the 1°PhAO is likely to adsorb on to the silica more strongly than the phosphite. A similar situation was also apparent in Jones' study [24, 30] in which thioester / hindered phenol combinations were investigated in PP. The same gel silica was used and was found to provide a similarly weak / ill-defined controlled release effect. In

Jones' study the adsorption activities of the hindered phenolic AO and the thioesters were found (by flow micro-calorimetry) to be similar, arguably too similar to allow effective controlled release of the hindered phenolic AO. The octa-functionality of the latter (four –OH groups and four ester groups per molecule) would also have impeded release – particularly if the adsorption of the thioester is of equal strength (per functional group) with lower functionality (two ester groups per molecule).

However, the stabilization and degradation of the polymer are not the only parameters that affect the impact strength of rotationally molded samples. The crystalline content and spherulite size distribution has an important effect on the impact strength of PP. Several authors have confirmed this [31, 32], and previous investigations indicated that a high degree of crystallinity and large spherulite sizes cause lower impact strength and brittle failures. Fast cooling rates avoid the formation of large spherulites and enhance high crystallinity content. Fast cooling of the mold by spraying it with water or applying other suitable cooling methods, could greatly improve the impact strength of the sample.

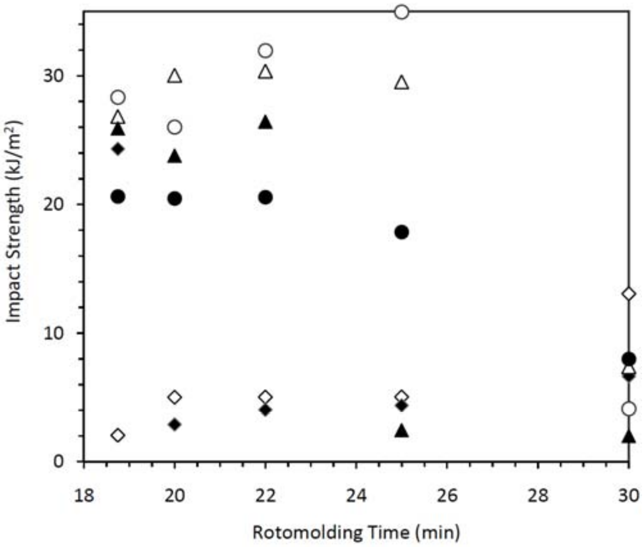

Figure 6: Un-notched impact strength of rotomolded samples against rotomolding time. ◇◆ unstabilized, △▲ hindered phenolic antioxidant, ○● hindered phenolic antioxidant combined with phosphite secondary antioxidant. Open symbols represent combinations without silica, solid symbols represent combinations with silica.

5. CONCLUSIONS

1. The carbonyl induction time (CIT) increases proportionally with the concentration of 1°PhAO until it reaches a limiting value of approximately 70 minutes, at a 1°PhAO level of 13250 ppm.

2. At 230°C, the 1°PhAO/HALS and the 1°PhAO/thioester-based secondary antioxidant blends were antagonistic at all ratios investigated. It was only the 1°PhAO/phosphite based antioxidant blend that was synergistic under these conditions. The maximum synergy was observed at 1°PhAO/phosphite antioxidant ratios between 1:1 and 2:1.

3. The addition of gel silica (a potential controlled release agent for the stabilizers) has not, in this investigation, been beneficial in terms of enhancing stability during the rotational molding process. Controlled stabilizer release did not occur to any useful degree.

4. The primary hindered phenolic antioxidant in combination with the secondary phosphite-based antioxidant in a 2:1 ratio at a total concentration of 6000 ppm provided the best balance between stabilization and impact strength, and offers an economical workable solution to employ PP in rotational molding applications.

ACKNOWLEDGEMENTS

The authors thank the Manchester Metropolitan University (MMU) for the opportunity given to carry out the research and the financial support for this project.

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Received on 08-10-2015 Accepted on 06-11-2015 Published on 12-01-2016

DOI: http://dx.doi.org/10.6000/1929-5995.2015.04.04.2